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Ti nanoparticles were produced using a cluster-deposition method. Ti:TiO core-shell structures were fabricated by partially oxidizing the surface of the Ti nanoparticles produced by a cluster-deposition system via multistep annealing at 250 °C in oxygen. X-ray diffraction and transmission-electron microscopy studies reveal an increase in the thickness of the TiO shell with increasing annealing time. The magnetic moment and the coercivity of the core-shell nanoparticles increase with the TiO shell thickness, which is consistent with homogenous bulk defects in TiO. The core-shell nanoparticles display an abnormal hysteresis loop, which probably reflects a combination of antiferromagnetic exchange and magnetocrystalline anisotropy. © *2010 American Institute of Physics*. [doi:10.1063/1.3359423]

Room temperature ferromagnetism[1] has been reported in a group of oxide thin films including ZnO, MgO, TiO_2, and others. Previous works have focused on uniformly oxidized thin films.[1] There has not been any report on the formation of metal-metal oxide core-shell nanoparticles during gradual oxidation and the evolution of magnetism during this process. This type of system can provide information on the location and evolution of magnetic moment and exchange coupling mechanism. There are several studies that show the essential role of defects in room temperature ferromagnetic oxides,[2–10] and TiO,[11] with 15% random vacancies on both Ti and O sites (or bulk defects), provides an ideal system for investigating defects and magnetism in an otherwise rarely studied nanoparticle material. Fully oxidized rock-salt TiO nanoparticle film has been previously produced with a cluster-deposition system via *in situ* oxidation[2] and the film shows ferromagnetism up to 400 K. In this work, we will focus on Ti:TiO core-shell nanoparticles with hexagonal TiO shell.

Ti nanoparticles were produced using a cluster-deposition method[12] and deposited on Si (100) substrates and carbon coated Cu-grids. The as-deposited Ti nanoparticles were then annealed at 250 °C in O_2 for consecutive 10 min periods. After each 10 min annealing period, structural and magnetic properties of the Ti nanoparticles were investigated using x-ray diffraction (XRD) and transmission electron microscopy (TEM), and superconducting quantum interference device magnetometry (SQUID).

XRD patterns of the as-deposited and annealed Ti nanoparticles for different times are shown in Fig. 1. The standard diffraction peaks corresponding to hexagonal Ti and TiO structures are indicated as dashed and dotted lines, respectively. The as-deposited sample corresponds to hexagonal Ti [curve (a) in Fig. 1]. In contrast, after annealing in O_2 at 250 °C for 10 min, the diffraction peak corresponding to the (110) plane of the hexagonal TiO structure appears along with a remaining Ti (101) peak [curve (b) in Fig. 1]. The intensity of the TiO (110) peak increases with increasing annealing time and completely dominates after 50 min of annealing at 250 °C [curve (d) in Fig. 1].

The XRD results are consistent with TEM (Fig. 2) analysis. The as-deposited Ti nanoparticles have an average diameter of 27 nm and clean surface (Fig. 2). However the inset shows the formation of a 5-nm-thick shell at the surface after 10 min annealing in O_2. The Ti core shrinks with increasing annealing time and disappears after 50 min of annealing.

The magnetic properties of the Ti:TiO core-shell nanoparticles were studied as a function of the annealing time. Figure 3(a) shows a typical hysteresis loop for Ti:TiO nanoparticles (annealed in O_2 at 250 °C for 20 min). Note that the paramagnetic background is possibly due to isolated paramagnetic spins. The measured magnetic parameters as a function of the annealing time are summarized in Fig. 3(b). The increase in coercivity (H_c) and moment (M_s) with the increase in annealing time (or thickness of the TiO shell as verified by TEM and XRD) indicates bulk moment, which is consistent with the bulk defects of TiO.

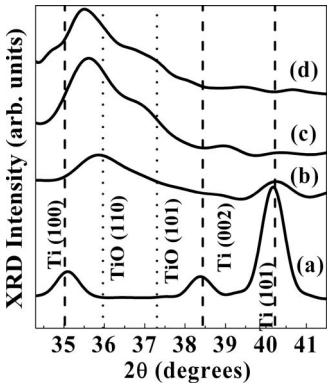

FIG. 1. Cu $K\alpha$ XRD patterns of (a) as-deposited Ti nanoparticles and Ti:TiO core-shell nanoparticles prepared by annealing of Ti nanoparticles in O_2 at 250 °C for different times: (b) 10, (c) 30, and (d) 50 min. Dotted and dashed lines show the standard peak positions of hexagonal TiO and hexagonal Ti, respectively.

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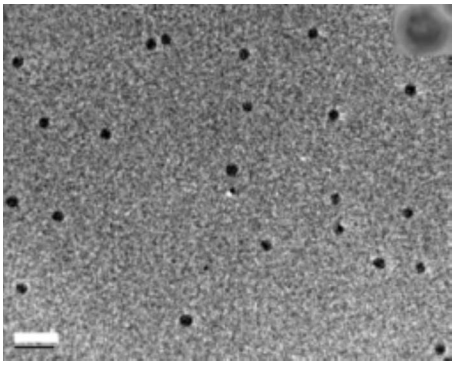

FIG. 2. TEM image of the as-deposited Ti nanoparticles having an average particle size of 27 nm, the scale is 100 nm. The inset shows the formation of the Ti:TiO core-shell structure after annealing the Ti nanoparticles in O_2 at 250 °C for 10 min.

The origin of the magnetic moment in undoped oxides has been attributed to cation[5,6,9] and oxygen vacancies.[5–8] Since TiO is rich in both Ti (V_{Ti}) and oxygen (V_O) vacancies, the exact contribution from each still needs further investigation. Note that, in other oxide thin films without bulk defects, the magnetic moment was attributed to surface defects.[2,13] The decrease in the moment and coercivity during the last 10 min annealing is probably due to an annihilation of V_O (Refs. 3 and 4) or conversion of TiO into a mixture of TiO and other minority phases.

An interesting feature of the hysteresis loop is a counterintuitive moment jump (δM) triggered at a singularity field H_o, as clearly shown in Fig. 3(a). δM increases for the first 20 min and then, decreases at intermediate annealing steps and is completely absent in the fully oxidized nanoparticles [Fig. 3(b)]. This variation is synchronized with the initial increase and subsequent decrease in the interfacial area (or volume). Thus δM can be correlated with the net moment of unstable interfacial spins. The net moment is originally aligned in a metastable direction against the filed. As field decreases, the spins flip to relatively stable directions resulting in the net moment along the field. This mechanism is illustrated in Fig. 3(c), where the abnormal loop shape can be reproduced by the superposition of a soft hysteresis loop (produced by the TiO shell) and a square-shaped loop representing the behavior of the interfacial spins. Interestingly, H_o and δM have opposite variation trends, the origin of which still needs further investigation.

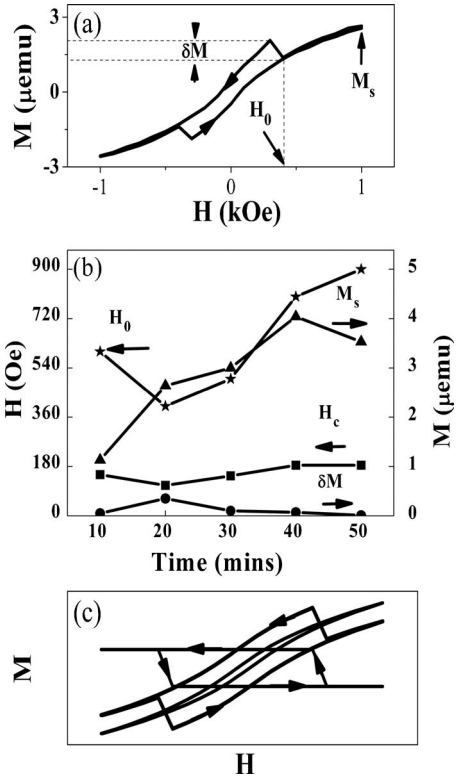

FIG. 3. Magnetic properties of Ti:TiO core-shell nanoparticles: (a) hysteresis loop after the second 10 min annealing, (b) time dependence of the coercivity H_c (squares), triggering field H_0 (stars), moment M_s (triangles), and magnetization jump δM (circles), and (c) superposition of a soft hysteresis and a square-shaped loop to produce the abnormal loop.

Abnormal moment jump was previously detected in the magneto-optic Kerr effect (MOKE) hysteresis loops of Co-implanted rutile (001) TiO_2,[14] while it was absent in corresponding SQUID hysteresis loops. This was attributed to the sensitivity of MOKE to surface, in-plane anisotropy and transverse components of magnetization.[14] Interestingly, comparison of the MOKE loops[14] to ours reveals a similar correlation between δM and H_o. Note that this effect was restricted to the (001) cut rutile TiO_2 with fourfold anisotropy and was absent in its (100) cut counterpart with twofold anisotropy.[14] It is obvious from the MOKE loops[14] that the effect is more pronounced along the axis, higher symmetry might have favored its observation. Similarly the abnormal moment jump is only observed in our Ti:TiO core-shell particles with hexagonal TiO shell while it is absent in those with rock-salt TiO shell. Since the symmetry of anisotropy strongly depends on the crystallographic structure, the hexagonal TiO shell most likely has a sixfold anisotropy as observed in hexagonal Co-doped ZnO.[15] Though the exact mechanism leading to the unusual moment jump is unknown, a possible explanation might involve AFM coupling and magnetic anisotropy. The core and shell have different vacancy concentrations and most likely different anisotropies. This combined with an AFM interaction between the core and shell might give rise to the abnormal moment jump. Without magnetic anisotropy, the net magnetization of the AFM coupled system would simply follow the external field, but different sublattice anisotropies may cause sublattice spin jumps in a direction opposite to the external field.[16] The unusual features in the loops occur at fields of about 0.5 kOe, which gives the order of magnitude of the exchange fields. This is consistent with our past analysis of exchange interaction in Co:CoO core-shell structures.[17] The AFM interactions may be caused by RKKY interactions in the oxide phase[9] or through the Ti core.

In conclusion, Ti:TiO core-shell clusters with increasing shell thicknesses were fabricated by annealing the Ti nanoparticles produced with a cluster-deposition method in O_2 at 250 °C for increasing time. The magnetic moment increases with the growing TiO shell, consistent with the bulk defects in TiO. The core-shell nanoparticles exhibit abnormal hysteresis loops probably due to magnetocrystalline anisotropies in combination with AFM interactions at the interface. How-

ever, spin structure and explanation of the magnetization jump needs further experimental and theoretical investigation.

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